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THE ROLE OF IMPURITIES IN DETERMINING THE PERFORMANCE OF PHOSPHORIC ACID MANUFACTURE BY THE HEMIHYDRATE PROCESS*

Prepared by

Norman Robinson**

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** Phosphates Development Manager, Licensing and Consultancy Services, Norsk Hydro Fertilizers Ltd., Levington Research Station, Levington, England

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SUMMARY

The mining of phosphate rock, and the beneficiation routes used, both affect the concentration of impurities present, and these in turn directly influence the processing characteristics of the rock.

In determining the optimum mining and beneficiation route consideration should be given to the effects these routes have on impurity levels, in addition to the more usual factors, such as P_2O_5 enrichment.

Due to the complex nature of the chemistry involved, it is not possible to quantify the effects of impurities without thoroughly testing a rock, using techniques which model the process route to be used.

This paper outlines the type of evaluation techniques required and considers the effects of impurities on the performance of the energy saving Hemihydrate process route.

Introduction

The primary component of a mined phosphate rock is Fluorapatite which occurs in nature in association with igneous rocks, or more commonly as phosphorites combined with sedimentary rocks. Other forms of apatite such as Hydroxyapatite and Chlorapatite are also found but these are less common, particularly the latter.

The mining methods used are largely dependent on the depth and nature of the overburden. These may involve open cast methods using scrapers or drag lines, or it may be necessary to apply underground shaft and tunnel methods. The raw rock generally requires beneficiating before it is suitable for the manufacture of phosphoric acid. The methods employed generally depend on the nature of the associated impurities and minerals. The simplest method involves crushing and screening operations followed by density separations, using for example, hydrocyclones. The desired degree of upgrading cannot always be achieved by this method and more complicated and expensive procedures, such as flotation and calcination, have to be employed.

Phosphate rocks contain a wide range of impurities, none of which are completely removed by the beneficiation process. The need to beneficiate and the choice of method should not be dictated solely by the requirement to maximise P_2O_5 concentration. The removal of impurities can increase or reduce the performance of a phosphate rock when used for phosphoric acid manufacture. This is true for both Dihydrate and Hemihydrate processes and implies that the mining and beneficiation operations should ideally take into account the implications on processing characteristics if a technical overall optimum is to be achieved.

The assessment of phosphate rocks using laboratory and pilot plant techniques is an important link between the producer of a rock and the potential user.

It provides essential data which can be taken into account when optimising beneficiation procedures and give guidelines to the suitability of a process route and the choice of operating condition.

In developing both Dihydrate and Hemihydrate phosphoric acid processes, Norsk Hydro Fertilizers UK, has extensive experience in the field of rock testing which covers a period of over 27 years. This paper outlines the more important aspects of the test procedures used and the effects of impurities on the performance of phosphoric acid manufacture by the Hemihydrate route.

Impurities Present in Phosphate Rocks

Phosphate rocks are usually found in association with silica minerals such as quartz, clays, serpentine, pyroxenes and micas. Carbonate minerals such as calcite or dolomite are also common and the choice of the beneficiation process is usually dictated by the requirement to remove these major impurities.

The remaining impurities are present in minor and in trace amounts. Many of these can affect processing characteristics and need to be taken into account when evaluating the beneficiation process.

Table 1 gives the range of impurities normally present in phosphate rocks together with the range of concentrations which can be encountered. It is important to bear in mind that of the impurities which normally affect processing performance, the relative effects, will not only be influenced by the amounts of impurities present, but also on the reactivity of the minerals which provide these impurities. The impurities produce charged ions which compete to attract other ions and produce compounds which can precipitate or be evolved in the off gases. Which type of "ion trapping" predominates will depend on the rates of formation of the individual ions as well as the concentrations produced. This kinetic effect is the main reason why it is very difficult to predict the performance of a phosphate rock when used to manufacture phosphoric acid. With experience, general behaviour patterns can be predicted, but to quantify

sufficiently for plant design, or evaluate the economic implications of changing rock sources, it is necessary to determine performance parameters experimentally.

The effect of Impurities on Hemihydrate Process Performance

In broad terms the effects of impurities are similar for both the Hemihydrate and Dihydrate processes. However, there are important differences which are mainly due to the reaction conditions used when producing hemihydrate.

A summary of the most important effects are as follows:

Carbonates

Calcite or dolomite are the usual minerals which provide carbonate. During acidulation of the rock the carbonate will decompose producing carbon dioxide which is evolved in the off gases. In the Hemihydrate process the acid P_2O_5 concentration can be controlled between 40% and 50% which gives the acid a higher density and viscosity compared to the acid produced by a Dihydrate process. The increase in viscosity causes more entrainment of the CO_2 and the acid in the reactor becomes "gassed". Defoamer can be used as a means of control. Mechanical foam breakers are less effective unless these produce a large turn-over of slurry surface. It is important to minimise the gassing level as this eventually has an adverse effect on hemihydrate crystal growth. Gassing levels of up to 20% are usually not harmful. The other effect caused by entrainment of CO_2 is that it causes a reduction in reactor operating levels during short shutdowns of the plant. On start-up this change in level has to be considered if good sulphate control is to be maintained. Organic matter present in rock can also reduce the rate of de-entrainment and affect the effectiveness of defoamers. This effect has sometimes been noticed with calcined rocks, rarely with others. If a significant proportion of the carbonate is present in the apatite structure, as in Francolite, then its decomposition can cause disintigration of the rock grains and increase the reaction rate.

Silica

This is one of the most common impurities present in rocks and is usually present in the form of quartz or clays with sometimes minor quantities of micas, pyroxenes and serpentines. Quartz reacts slowly in phosphoric acid containing fluorine, whereas silica in clays react readily. The availability of reactive silica determines the extent of fluorine evolution and the availability of fluoride ions to trap metallic cations such as calcium and aluminium. The ionic reaction involving aluminium affects hemihydrate crystal properties and filterability. In rare cases where there is a deficiency of silica the concentration of fluoride can increase which can produce increased corrosion rates in a phosphoric acid plant. Some low P_2O_5 grade rocks contain high levels of silica, most of which is relatively unreactive. In these cases the waste silica can constitute a significant proportion of the solids which are filtered and in consequence can affect filterability. For example, if the silica is coarse then it can act as a filter aid and improve filtration. If as a result of beneficiation, or grinding at the user plant, the silica is in a finely divided state, then this can blind the filter cake and reduce filterability.

Fluorine

All phosphate rocks apart from chlorapatites contain fluorine within the apatitic structure. It plays a significant part in the chemistry of phosphoric acid manufacture, both Hemihydrate and Dihydrate. In the Hemihydrate process the higher reaction temperature and P_2O_5 concentration produces more evolution of the fluorine as SiF_4 from the reaction system compared to the Dihydrate process. The higher reaction temperature also favours the decomposition of the SiF_6^{--} ion to F^- which in turn reacts with calcium ions and aluminium ions to produce compounds or complexes which are removed with the hemihydrate. As already mentioned the aluminium fluoride complex ion can influence the crystal properties of the hemihydrate and its filterability. Due to the complexing of part of the aluminium the Hemihydrate process produces an acid which has a lower aluminium concentration compared to the Dihydrate process from a given rock. Fluorine

together with silica are responsible for the formation of fluorsilicate scales in both processes.

Metallic Impurities

Cationic impurities can affect processing performance in several ways. The influence of aluminium on hemihydrate filterability has already been mentioned. Iron and Magnesium have little effect on crystal properties, but they can affect acid viscosity which in turn influences filtration rates. Complex compounds can also be produced which precipitate slowly and form sludge in acid storage tanks and occasionally even in the filter return acid tanks. Blinding of filter cakes and cloths also occurs but only in rare cases where impure rocks are processed containing high concentrations of Magnesium, Iron and Aluminium.

Alkali metals combine with SiF_6^{--} ions to produce silicofluorides which can form scale. This occurs in both Dihydrate and Hemihydrate processes but there are important differences in behaviour. Due to the higher acid P_2O_5 concentration in the Hemihydrate process the solubility of Na_2SiF_6 is very low and unlike the Dihydrate process this eliminates any tendency for scale to occur in reaction vessels and pipework handling slurry. On the filter the higher acid P_2O_5 concentration increases the driving force for silicofluoride scaling and the degree of scaling depends on the concentrations of alkali metals present in the rock.

Test Procedures

The test methods used at Levington vary in complexity from analysis and simple laboratory tests to continuous pilot plant operation for the production of phosphoric acid. The scope of the test work will depend on the state of the project, which may be preliminary, intermediate or advanced. For example, in the case where a new rock deposit is being evaluated, a large number of samples may be involved, originating from core samples taken from different parts of the deposit, or produced by different beneficiation routes. In this case preliminary laboratory tests would be the quickest and most cost effective approach. Where the rock composition is defined, and the mining and beneficiation routes finalised,

it is necessary to quantify the important processing parameters which affect the economics of phosphoric acid manufacture by a full pilot plant evaluation. Other examples fall between these two extremes and are planned accordingly to provide the required information with the minimum of cost.

Detailed descriptions of the main test procedures used have already been published (1, 2) and it is only possible within the scope of this paper to give a brief outline of the most important techniques.

The selected test procedure will involve some or all of the following tests:

Sampling

A representative sample must be obtained before any test work is carried out. Normally the rock is shipped in several containers and these should be emptied and the whole consignment mixed until homogeneous.

Physical and Chemical Properties

A sample of the mixed rock is analysed by X-ray diffraction, atomic absorption and chemical methods for all compounds likely to influence its behaviour. Particle size and distribution are important since these factors can affect the rate of reaction, which in turn can influence reaction control, P_2O_5 efficiency and filterability. A complete sieve analysis is carried out on all samples which have been prepared for specific tests.

Reactivity

The reactivity of a rock can be determined by a batch or a continuous test. The batch technique is a simple dissolution test using phosphoric acid and sulphuric acids and rocks having a constant size fraction. A continuous test can be used to determine the level of unreacted rock directly for a given set of operating conditions.

Foaming

To assess the degree of foaming which a rock may produce, a standard sieve fraction is acidulated with phosphoric acid. The height of foam produced is

plotted against time and the area under the curve is calculated. This area is termed the "Foam Stability Index" and is compared with values obtained from other rocks whose foaming characteristics on a full scale plant are known.

Crystallisation Tests

These are laboratory tests and involve continuous acidulation of phosphate rock in two or more stirred tank reaction vessels. The laboratory unit provides comparative data on crystal properties and filtration rate and its main purpose is to obtain an indication of expected performance and to screen rock samples if several are involved. This type of unit is also used for development work and in particular in the basic study of the effects of impurities on crystal properties.

Pilot Plant Tests

Although laboratory tests give valuable guidelines on raw material selection and performance, the data produced are largely comparative and must be quantified on a pilot plant. In any pilot plant trial the operation is continuous over a period of at least 100 hours. The reactor residence times and operating conditions are the same as would be used on a full scale plant and no evaluation of results is carried out until equilibrium has been reached.

Pilot plants can be used to compare the performance of rocks under a given set of operating conditions. They can also be used to optimise operating conditions for a given rock.

The following illustrates the type of information provided by a typical pilot plant trial:

(a) Magnitude and type of P_2O_5 loss. P_2O_5 efficiency.

(b) Expected filter loading using different types of filter.

(c) Sulphuric acid, defoamer and other chemical additive consumptions.

(d) Compositions of rock, acid and hemihydrate and expected proportionation of impurities.

(e) Process Heat and Mass Balance.

Post Pilot Plant Tests

Following the pilot plant investigation further tests are frequently carried out to provide additional data for plant design and/or the manufacture of phosphatic intermediates. These could involve:

Settling Tests

Any solid which is precipitated with time from the product acid is quantified and identified.

Corrosion Tests

Phosphoric acid produced from different rocks can often produce widely different corrosion rates when in contact with alloy steels. The impurities which have the greatest effect on corrosion are Chloride, Fluoride and reducing agents such as Sulphides. Static corrosion tests are carried out using pilot plant acid and standard alloys commonly used to fabricate phosphoric acid plants.

Physical Properties

Measurements of density, viscosity or vapour pressure are made on the product acid to provide design data.

Preparation of Ammonium Phosphates and Triple Superphosphate

These intermediates are prepared in the laboratory to provide product compositions.

References

1. Robinson N. "The Assessment of Phosphate Rocks for Phosphoric Acid and Ammonium Phosphate Manufacture". Phosphorous and Potassium No. 57, January/February 1972.

2. Robinson N. "Laboratory and Pilot Plant Assessment of Phosphate Rocks for Phosphoric Acid and Ammonium Phosphate Manufacture". I.S.M.A./A.N.D.A. Technical Conference Sao Paulo, 1972.

Table 1 Typical Impurities Present in Phosphate Rocks (% w/w)

Impurity	Range	Impurity	Range
CaO	22-55	SO_4	0-4
SiO_2	0.1-35	CO_2	0.05-8
Fe_2O_3	0.1-3	Organic	0-0.6
Al_2O_3	0.1-3	SrO	0-2
MgO	0.1-2	U_3O_8	0.0008-0.02
Na_2O	0.03-1.5		
K_2O	0.01-0.3		
Cl	0.003-0.15		

In addition to the above a large number of trace elements occur including Cu, As, Cr, Cd, Rare Earths, Ni, Hg etc.